DOCKET NO: 291453US0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF	:
PHILIPPE KRAFFT, ET AL.	: EXAMINER: ROSALYND KEYS
SERIAL NO: 10/580,003	:
FILED: DECEMBER 19, 2006	: GROUP ART UNIT: 1621
FOR: PROCESS FOR PRODUCING DICHLOROPROPANOL FROM GLYCEROL, THE GLYCEROL COMING EVENTUALLY FROM THE CONVERSION OF ANIMAL FATS IN THE MANUFACTURE OF BIODIESEL	:

DECLARATION

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

Now comes Patrick Gilbeau, who deposes and states as follows:

1. I am an inventor of the above-identified application for U.S. patent.

2. I understand English.

3. I understand that the main claim in the above-identified application is Claim 77, which has been amended to read as follows:

77. A process for producing dichloropropanol, comprising subjecting glycerol to a reaction with a chlorinating agent in the presence of a carboxylic acid catalyst to produce dichloropropanol, wherein the carboxylic acid is selected from the group consisting of mono carboxylic acids containing 5 or 6 carbon atoms, dicarboxylic acids selected from glutaric acid and adipic acid, and poly carboxylic acids selected from tri- and tetra-carboxylic acids.

4. The following further testing was done:

1. Testing of di- tri- and tetracarboxylic acids
1.1. Testing of succinic, glutaric and adipic acids (~ 1 mol of dicarboxylic acid per kg)

526 g of 3-chloro-1,2-propanediol (4.76 mol), 51.6 g of an azeotropic mixture of hydrogen chloride and water (HCl 6 N) and 1.079 mol of dicarboxylic acid have been introduced in a 1.8 l double-wall glass reactor fitted with a mechanical stirrer, a distillation column, a temperature probe and feed lines for glycerol and hydrogen chloride solution. The reaction mixture has been heated up to 125 °C under stirring. When the temperature has reached 125 °C, the reactor has been continuously fed with glycerol and with an aqueous solution containing 37 % by weight of hydrogen chloride (2 molar equivalents according to glycerol). The mixture which distilled off has been condensed through a refrigerant connected to the distillation column and has been collected in a 1 l decanter previously filled with an aqueous solution saturated with 1,3-dichloropropane-2-ol (157 g of dichloropropanol mixed with 893 g of deionized water). A part of that aqueous phase has been sent to the reflux of the distillation column at a fixed rate adapted to recover all the dichloropropanol formed by the reaction (8.45 ml/g of glycerol fed). The decanter has been fitted with a bottom valve to recover the dense organic phase which separated during the reaction and an overflow outlet to recover the aqueous phase. Rates of production of dichloropropanol (**DCPol**) in the organic and aqueous phases have been obtained from weightings of phases with time and gas phase chromatography (GPC) analysis. By-products (diglycerol and cyclic diglycerol, chlorohydrins of diglycerol and of cyclic diglycerol) production rate have been obtained by GPC analysis of the reactor residue.

The feeding rates of glycerol and of the aqueous solution containing 37 % by weight of hydrogen chloride have been set at the highest possible values to keep a nearly constant liquid level in the reactor (identical for each test). For such conditions, the reactor operated under stationary regime with the catalyst operating at its maximal capacity and the reactor performances were stable with time on stream.

Table 1 hereafter summarizes the DCPol productivity (g/h/kg of reaction medium), the by-products production (g/g of DCPol) and the catalyst concentration (g/kg) found in the decanter aqueous and organic phases, measured in the tests with succinic, glutaric and adipic acid after respectively 12.5 h, 14 h and 19.1 h of time on stream.

Table 1

	succinic acid	glutaric acid	adipic acid
DCPol (g/h/kg reaction medium)	96.7	122.1	121.1
By-products (g/g DCPol)	0.012	0.013	0.009
Catalyst in aqueous phase (g/kg)	< 0.02	< 0.01	n.d.
Catalyst in organic phase (g/kg)	< 0.2	< 0.1	n.d.

n.d. = not detected

1.2. Testing of succinic, glutaric, adipic and azelaic acids (~ 2 mol of dicarboxylic acid per kg)

The test conditions have been the same as for the previous tests but with a concentration of dicarboxylic acid in the reaction medium fixed at nearly 2 mol/kg.

Table 2 hereafter summarizes the DCPol productivity (g/h/kg of reaction medium), the by-products production (g/g of DCPol) and the catalyst concentration (g/kg) found in the decanter aqueous and organic phases, measured in the tests with succinic, glutaric, adipic and azelaic acids after respectively 15.9 h, 17.8 h, 21.0 and 16.4 h of time on stream.

Table 2

	succinic acid	glutaric acid	adipic acid	Azelaic acid
DCPol (g/h/kg reaction medium)	133.5	158.8	159.0	143.8
By-products (g/g DCPol)	0.005	0.008	0.007	0.005

1.3. Tri- (citric) and tetra (butane) tetracarboxylic acids

526 g of 3-chloro-1,2-propanediol (4.76 mol), 51.6 g of an azeotropic mixture of hydrogen chloride and water (HCl 6 N) and 1.079 mol of carboxylic acid have been introduced in a 1.8 l double-wall glass reactor fitted with a mechanical stirrer, a distillation column, a temperature probe and feed lines for glycerol and hydrogen chloride solution. The reaction mixture has been heated up to 125 °C under stirring. When the temperature has reached 125 °C, the reactor has been continuously fed with glycerol and with an aqueous solution containing 37 % by weight of hydrogen chloride (2 molar equivalents according to glycerol). The mixture which distilled off has been condensed through a refrigerant connected to the distillation column and has been collected in a 1 l decanter previously filled with an aqueous solution saturated with 1,3-dichloropropane-2-ol (157 g of dichloropropanol mixed with 893 g of deionized water). A part of that aqueous phase has been sent to the reflux of the distillation column at a fixed rate adapted to recover all the dichloropropanol formed by the reaction (8.45 ml/g of glycerol fed). The decanter has been fitted with a bottom valve to recover the dense organic phase which separated during the reaction and an overflow outlet to recover the aqueous phase. Rates of production of dichloropropanol (DCPol) in the organic and aqueous phases have been obtained from weightings of phases with time and gas phase chromatography (GPC) analysis. By-products (diglycerol and cyclic diglycerol, chlorohydrins of diglycerol and of cyclic diglycerol) production rate have been obtained by GPC analysis of the reactor residue.

The feeding rates of glycerol and of the aqueous solution containing 37 % by weight of hydrogen chloride have been set at the highest possible values to keep a nearly constant liquid level in the reactor (identical for each test). For such conditions, the reactor operated under stationary regime with the catalyst operating at its maximal capacity and the reactor performances were stable with time on stream.

Table 3 hereafter summarizes the DCPol productivity (g/h/kg of reaction medium), the by-products production (g/g of DCPol) and the catalyst concentration (g/kg) found in the decanter aqueous and organic phases, measured in the tests with citric acid (a tri-carboxylic acid according to the invention) and butane tetracarboxylic acid after respectively 25.7 h and 20.2 h of time on stream.

Table 3 – Tri- and tetracarboxylic acids

	citric acid	Butane tetracarboxylic
DCPol (g/h/kg reaction medium)	32.3	36.3
By-products (g/g DCPol)	0.027	0.033
Catalyst in aqueous phase (g/kg)	0.04	0.01
Catalyst in organic phase (g/kg)	0.05	0.12

5. The technical problem the invention described in Claim 77 above solves is to provide a process for manufacturing dichloropropanol which minimizes by-product formation and minimizes catalyst loss from the reaction medium. This is shown both in the above-identified application for U.S. patent as originally filed and in the additional testing described above when the catalysts according to the invention are used. See for example the test results shown at Table 2, page 28, where improvements using adipic acid over acetic acid (a catalyst described in, e.g., DE 197308 and Britton (U.S. 2,144,612)) are apparent.

Indeed, comparison of tests 3 (acetic acid) and 11 (adipic acid) in Table 2, page 28 of the original application, show that with adipic acid, hydrogen chloride and glycerol conversion rates are higher, dichloropropanol selectivity is substantially higher, and the loss of catalyst in the distillate is reduced to almost nothing vs. 55%. These results could not have been expected for instance from DE 197308 where acetic acid is shown to be the best of the carboxylic acids tested (examples 1 and 2). The skilled man would have no incentive to select the catalysts of Claim 77 to obtain better results vis-a-vis by-product formation and catalyst loss in the process of the invention.

6. Table 1 above summarizes the results of a first set of continuous runs for glycerol chlorination carried out in the presence of succinic acid (DE 197308), glutaric acid and adipic

acid (present invention catalysts). The tests have been carried out for similar catalyst concentrations. The results indicate a dichloropropanol productivity (expressed as g dichloropropanol per h and per kg of reaction medium) at least 25% higher for glutaric and adipic acid with respect to succinic acid at full catalyst capacity, with no detectable loss of catalyst and similar or lower by-product formation (expressed in g of by-product per g of produced dichloropropanol).

Table 2 above summarizes the results of a second set of continuous runs for glycerol chlorination carried out in the presence of succinic acid, azelaic acid (DE 197308), glutaric acid and adipic acid (present invention catalysts). The tests of this run have been carried out for similar catalyst concentrations but higher than those used for the first run. The results indicate a dichloropropanol productivity (expressed as g dichloropropanol per h and per kg of reaction medium) between 11 and 40% higher for glutaric and adipic acid with respect to succinic and azelaic acid at full catalyst capacity, with no detectable loss of catalyst and similar or lower by-product formation (expressed in g of by-product per g of produced dichloropropanol).

7. The superior results obtained for glutaric acid and adipic acids, dicarboxylic acids with 5 and 6 carbon atoms, could not have been expected from DE 197308 where it can be seen that succinic and azelaic acids, dicarboxylic acids with 4 and 9 carbon atoms show equivalent yields for the glycerol monochlorhydrin production (example 3).

8. Table 3 above shows the results obtained with citric acid 2-hydroxypropane-1,2,3-tricarboxylic acid and 1,2,3,4-butanetetracarboxylic acid (both present invention catalysts). Tri- and tetra-carboxylic acids which are not to my knowledge mentioned in any prior references as catalysts for the reaction between glycerol and hydrogen chloride are clearly convenient catalysts for that reaction, with good productivities, low by-products formation and low losses of catalysts.

9. The undersigned petitioner declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believe to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

Patrick Gilbeau

Patrick Gilbeau

Signature

September 22, 2010

Date